

Electrospinning of Styrene-Isoprene Copolymeric Thermoplastic Elastomers

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(Received February 21, 2006; Accepted June 15, 2006; Published August 11, 2006)

ABSTRACT: In the present contribution, electrospinning of two chemically distinct thermoplastic elastomers based on block copolymers of styrene and isoprene [*i.e.*, multi-armed poly(styrene-*b*-isoprene) (PS-PI) and linear poly(styrene-*b*-isoprene-*b*-styrene) (PS-PI-PS)] was reported for the first time. Either 1,2-dichloroethane or chloroform was used as the solvent. The effects of solution concentration, solvent, applied electrical potential, chemical structure of the thermoplastic elastomers, and solution feed rate on morphological appearance and/or size of the as-electrospun products were investigated mainly by means of scanning electron microscopy (SEM). The electrospinnability of the polymer solutions was found to increase with increasing solution concentration. The size of the as-spun products from PS-PI solutions in 1,2-dichloroethane was consistently smaller than that of the products from the solutions in chloroform. The increase in the applied electrical potential caused the size of the as-spun products from both types of the polymer solutions to decrease monotonously or decrease with initial increase in the applied potential, reach a minimum at an intermediate value, and increase with further increasing applied potential. Despite the difference in the chemical structure of the two elastomers, the viscosity of their solutions in 1,2-dichloroethane was essentially similar, but the size of the as-spun products from PS-PI solutions was consistently larger than that of the products from PS-PI-PS solutions. [doi:10.1295/polymj.PJ2005234]

KEY WORDS Electrospinning / Thermoplastic Elastomer / Block Copolymer /

Thermoplastic elastomers are unique class of polymers which have physical and mechanical properties like vulcanized rubbers but can be processed by conventional thermoplastic processes.^{1,2} Typically, thermoplastic elastomers are block copolymers consisting of two or more chemically-distinct blocks that are covalently linked. Due to their chemical disparity, the different blocks tend to phase-separate into microdomains to minimize the overall free energy. This is in general the basic mechanism imparting these block copolymers their elastomeric behavior.^{3,4} Some of the common thermoplastic elastomers are segmented polyurethane, poly(styrene-*b*-butylene-*b*-styrene), poly(styrene-*b*-isoprene-*b*-styrene), and poly(styrene-*b*-isoprene).^{1–5} For examples, poly(styrene-*b*-isoprene-*b*-styrene) and poly(styrene-*b*-isoprene) are generally used for pressure sensitive applications, where durability and elasticity are important.^{4,5}

In recent years, electrostatic spinning or electrospinning has been viewed as a simple and versatile method for fabricating ultrafine fibers with diameters in the nanometer to sub-micrometer range.^{6–8} The heart of the technique is the use of a high electrical potential applying to a spinning liquid across a charged nozzle and a grounded screen collector. At right conditions, a charged stream of the spinning liquid was ejected and ultimately a mat of non-woven fibers

is collected on the collector.^{6–8} Various materials have successfully been electrospun into ultrafine fibers, *e.g.*, biopolymers, engineering plastics, conductive polymers, block copolymers, polymer blends, ceramics, and composite materials.^{9–12} There has not been much work on the electrospinning of thermoplastic elastomers, however.

Schreuder-Gibson *et al.* studied the transport properties of electrospun webs from a commercial cross-linkable thermoplastic polyurethane elastomer to be used as protective membranes for textiles.¹³ They found that the addition of electrospun layers onto melt-blown non-woven fabric substrates increased the resistance to air flow and aerosol protection without sacrificing the breathability of the composite fabrics. Nagapudi *et al.* demonstrated that the elastin-mimetic protein triblock copolymers could be produced with elastomeric- and plastic-like blocks in a manner analogous to synthetic thermoplastic elastomers, and these polymers could be fabricated in fiber form by electrospinning.¹⁴ Apart from these reports, there are no other works in the open literature that reports about the effects of solution and process parameters on morphological appearance of electrospun fibers from thermoplastic elastomers.

The present contribution reports, for the first time, the electrospinning of two chemically-distinct sty-

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rene-isoprene block copolymeric thermoplastic elastomers [*i.e.*, poly(styrene-*b*-isoprene) and poly(styrene-*b*-isoprene-*b*-styrene)]. The effects of some of the influencing solution and process parameters (*i.e.*, solution concentration, solvent, applied potential, chemical structure of the elastomers, and solution flow rate) on morphological appearance and/or size of the electrospun styrene-isoprene block copolymeric thermoplastic elastomeric products were investigated and reported.

EXPERIMENTAL

Materials

Multi-arm poly(styrene-*b*-isoprene) (PS-PI) (Aldrich, USA) and linear poly(styrene-*b*-isoprene-*b*-styrene) (PS-PI-PS) ($M_w \approx 140,000$ g/mol) (Aldrich, USA) in the form of pellets were used as model thermoplastic elastomers to be fabricated by electrospinning. The content of PS blocks within both elastomers was about 10 wt.%. 1,2-Dichloroethane [Lab-Scan (Asia), Thailand] and chloroform (Carlo Erba, Italy) were used as the solvents. Some important properties of the solvents are summarized in Table I.

Preparation and Characterization of Spinning Solutions

The PS-PI spinning solutions were prepared in either 1,2-dichloroethane or chloroform, while the PS-PI-PS solutions were prepared in 1,2-dichloroethane. A measured amount of PS-PI or PS-PI-PS pellets was dissolved in a measured quantity of the solvent to produce solutions with concentrations being 10, 15, and 20% w/v. The viscosity of the as-prepared solutions was determined by a Brookfield LVTDCP digital viscometer. These solutions were electrospun under various applied DC potentials in the range of 5 to 17.5 kV over a fixed collection distance of 10 cm. The collection time was also fixed at 1 min.

Electrospinning Process

Each of the as-prepared solutions was placed in a 50 mL plastic syringe. A blunt-end stainless-steel gauge 20 needle (*i.e.*, outside diameter = 0.91 mm) was used as the nozzle. The tilt angle of the syringe and the needle was 45° from a horizontal baseline to ascertain a constant presence of a solution droplet at

the tip of the nozzle. A sheet of aluminum foil on a plastic backing was used as the screen collector. A Gamma High Voltage Research DES30PN/M692 power supply was used to generate a high DC potential across the needle (connected to the positive emitting electrode) and the screen collector (connected to the grounding electrode). The feed rate of the solutions for most experiments was controlled by means of a Kd Scientific syringe pump at 3 mL/h, but, to study the effect of feed rate on the morphological appearance and/or size of the as-spun products, it was varied (*i.e.*, 3, 15, and 27 mL/h). The as-spun products were kept *in vacuo* for 24 h prior to further characterization to ensure the complete drying of the samples.

Morphological Observation

Morphological appearance and/or size of the as-spun products were examined by a JEOL JSM-5200 scanning electron microscope (SEM). Small pieces of the aluminum screen collector covered with the as-spun products were cut and pasted on a brass-stub by an adhesive tape. They were later coated with a thin layer of gold by a JEOL JFC-1100E ion-sputtering device prior to SEM observation. For the morphological appearance of the as-spun products, "fibers" was defined as the thread-like as-spun products exhibiting a high length to diameter ratio; "beads" was defined as the discrete droplets as well as droplet-like structure on the as-spun products, and "beaded fibers" was defined as the formation of beads with some traces of smooth fibers. The size of the as-spun products (either fibers or beads) was measured directly from the SEM images, with the average value being calculated from at least 50 measurements (for each spinning condition). The average number of beads per unit area (*i.e.*, the bead density) of the as-sprayed beads or the as-spun beaded fibers was calculated from selected SEM images (*i.e.*, 100x) through the division of the observed number of beads by the observation area (2,160 μm^2). Finally, the average number of fibers per unit area (*i.e.*, the fiber density) of the as-spun neat or beaded fibers was also calculated from selected SEM images (*i.e.*, 100x) through the division of the observed number of fibers by the observation area (2,160 μm^2).

RESULTS AND DISCUSSION

The model thermoplastic elastomers that were fabricated by electrospinning in this work were PS-PI and PS-PI-PS. Discrete beads, beaded fibers, and smooth fibers were common products from the electrospinning of these materials. Figures 1–3 show selected SEM images of the as-spun products obtained from the electrospinning of PS-PI in 1,2-dichloroethane

Table I. Some important properties of solvents used

Solvent	Boiling point (°C)	Surface tension (mN/m)	Density (g/cm ³)	Dipole moment (debye)	Dielectric constant
1,2-Dichloroethane	83.5	31.6	1.239	2.94	10.19
Chloroform	61.2	26.0	1.470	1.01	4.81

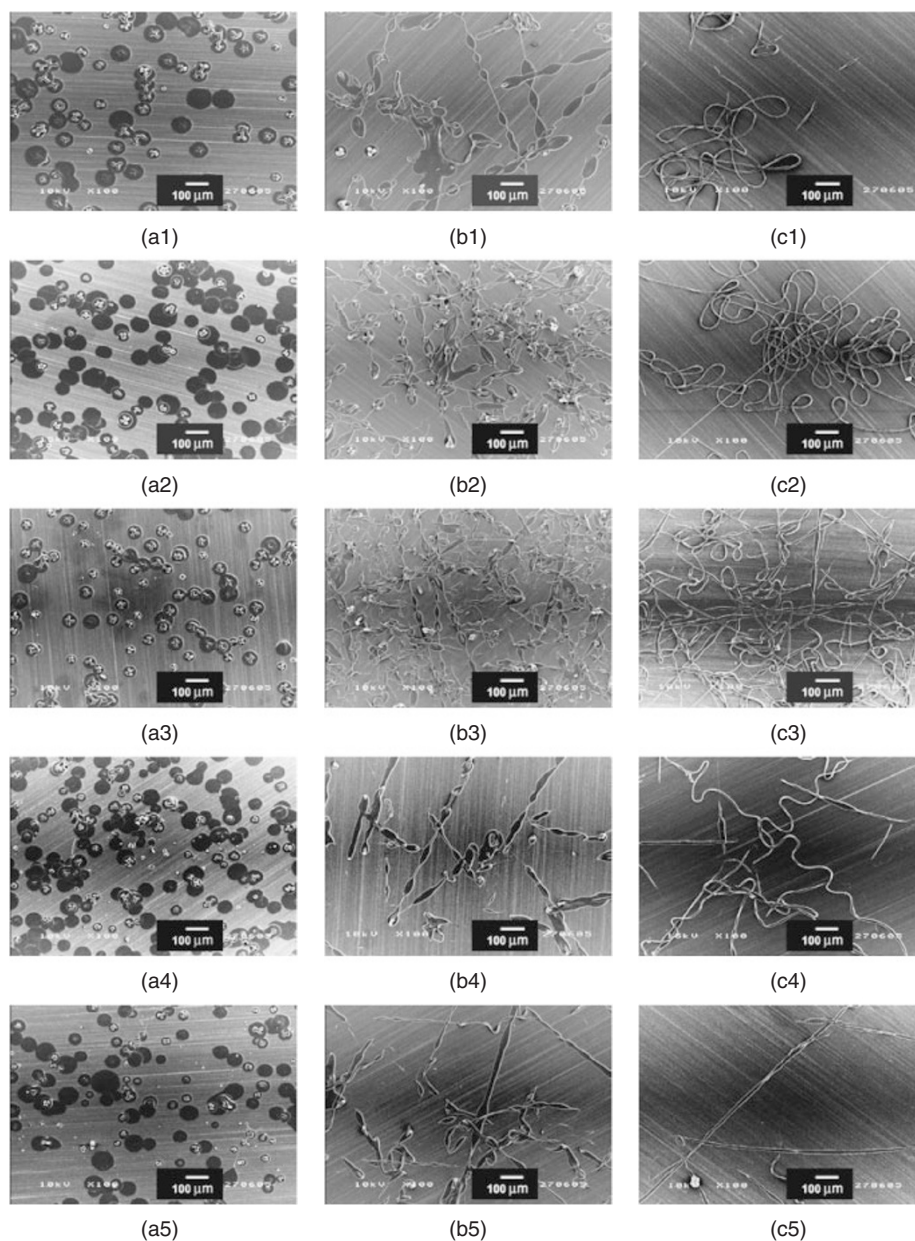


Figure 1. SEM images of the as-spun products from (a) 10, (b) 15, and (c) 20% w/v solutions of PS-PI in 1,2-dichloroethane. “1”, “2”, “3”, “4”, and “5” represent the applied potentials of 5, 7.5, 10, 12.5, and 15 kV, respectively, over a collection distance of 10 cm. The feed flow rate of the solutions was 3 mL/h.

and chloroform, and PS-PI-PS in 1,2-dichloroethane, respectively, at various solution concentrations and applied potentials. Moreover, quantitative analysis of these electrospun products was summarized in Tables II–V. Despite the fact that electrospinning is normally a technique capable of generating ultrafine fibers, the size of the as-spun products from PS-PI and PS-PI-PS solution was uncharacteristically large (*i.e.*, 2.7–16.0 μm). Such a peculiarity should be a result of the nature of these thermoplastic elastomers. Like other viscoelastic fluids, PS-PI and PS-PI-PS molecules are stretched out when they flow through the restricted channel of the nozzle. Upon leaving the nozzle’s exit, recoiling of the molecules occurs almost instantane-

ously. Such molecular recoiling for these thermoplastic elastomers may be so great that Coulombic stretching was not enough to finally thin down the diameters of the as-spun products.

Effect of Solution Concentration

Solution concentration is one of the most important parameters in electrospinning, due to its effect on viscosity. To prepare fibers by electrospinning, a proper solution concentration and hence the resulting viscosity is required. If the solution concentration is too low, a continuous stream of charged liquid (*i.e.*, charged jet) cannot be formed as the charged jet ultimately undergoes a flow-instability that results in the formation

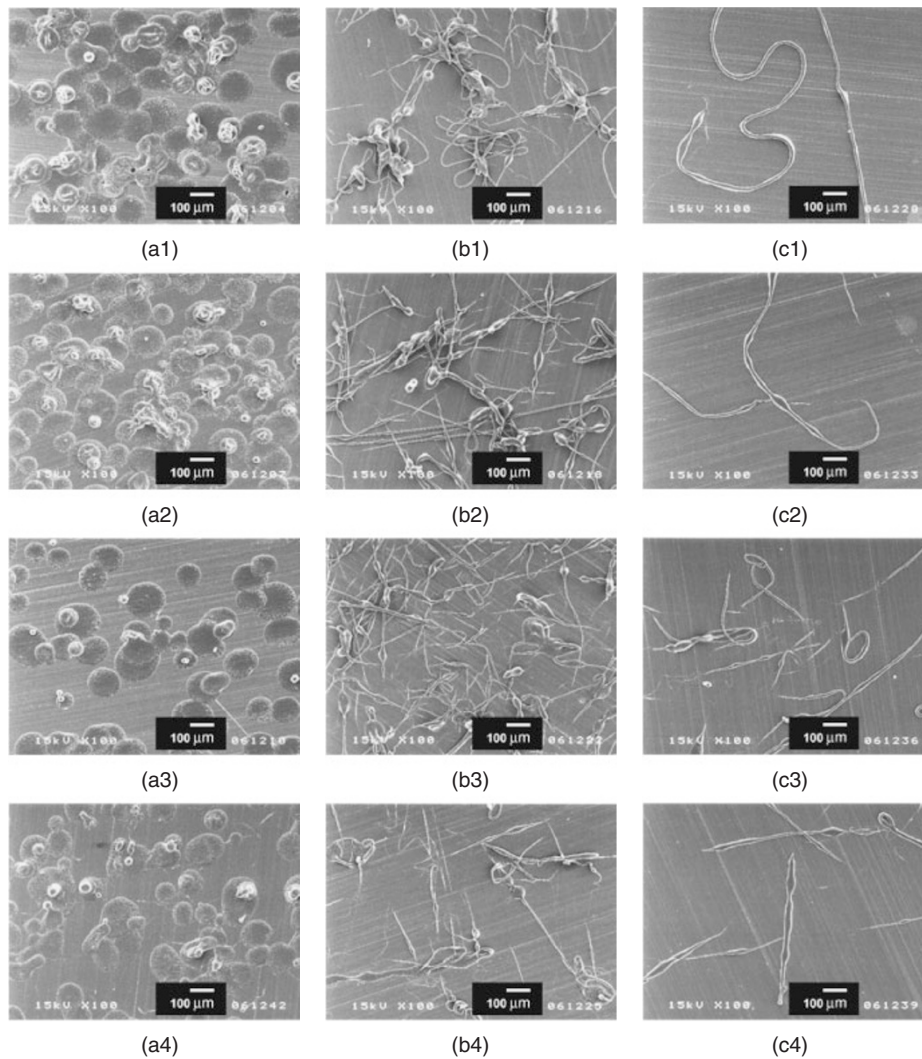


Figure 2. SEM images of the as-spun products from (a) 10, (b) 15, and (c) 20% w/v solutions of PS-PI in chloroform. “1”, “2”, “3”, “4”, and “5” represent the applied potentials of 5, 7.5, 10, 12.5, and 15 kV, respectively, over a collection distance of 10 cm. The feed flow rate of the solutions was 3 mL/h.

of droplets, a process traditionally known as electro-spraying.¹⁵ However, if the solution concentration becomes too great, electrospinning is also prohibitive as a continuous flow of the polymer liquid from the tip of the nozzle is somewhat restricted. As a result, there is a limited concentration or viscosity range within which a polymer solution can be electrospinnable. Beyond this range (either higher or lower), discrete droplets are likely to occur.¹⁶

In electrospinning, six types of forces are involved: they are 1) electrostatic which carries the charged jet from the nozzle to the screen collector, 2) Coulombic repulsion between adjacent charged species in a jet segment that is responsible for the stretching of the charged jet during its flight to the target, 3) body or gravitational, 4) viscoelastic which tries to prevent the charged jet from being stretched, 5) surface tension, and 6) drag due to the friction between the charged jet and the surrounding air.¹⁷ Table VI sum-

marizes the viscosity of the as-prepared PS-PI and PS-PI-PS solutions. Obviously, the viscosity increased monotonously with increasing solution concentration. At a low solution concentration or viscosity, the viscoelastic force was comparatively smaller than the Coulombic repulsion force, causing the charged jet to be over-stretched. The over-stretched jet broke up into smaller streams and later rounded up (due to the surface tension) to finally form discrete spherical droplets.¹⁷ As a result, irrespective of the type of the elastomer or solvent, electrospinning of the 10% w/v solutions only resulted in the formation of discrete beads (see Figures 1–3). On the other hand, at the highest solution concentration investigated (*i.e.*, 20% w/v), the charged jet did not break up and the rather smooth fibers were obtained. At an intermediate concentration (*i.e.*, 15% w/v) however, the formation of beaded fibers with or without occasional beads or rather smooth fibers was observed.

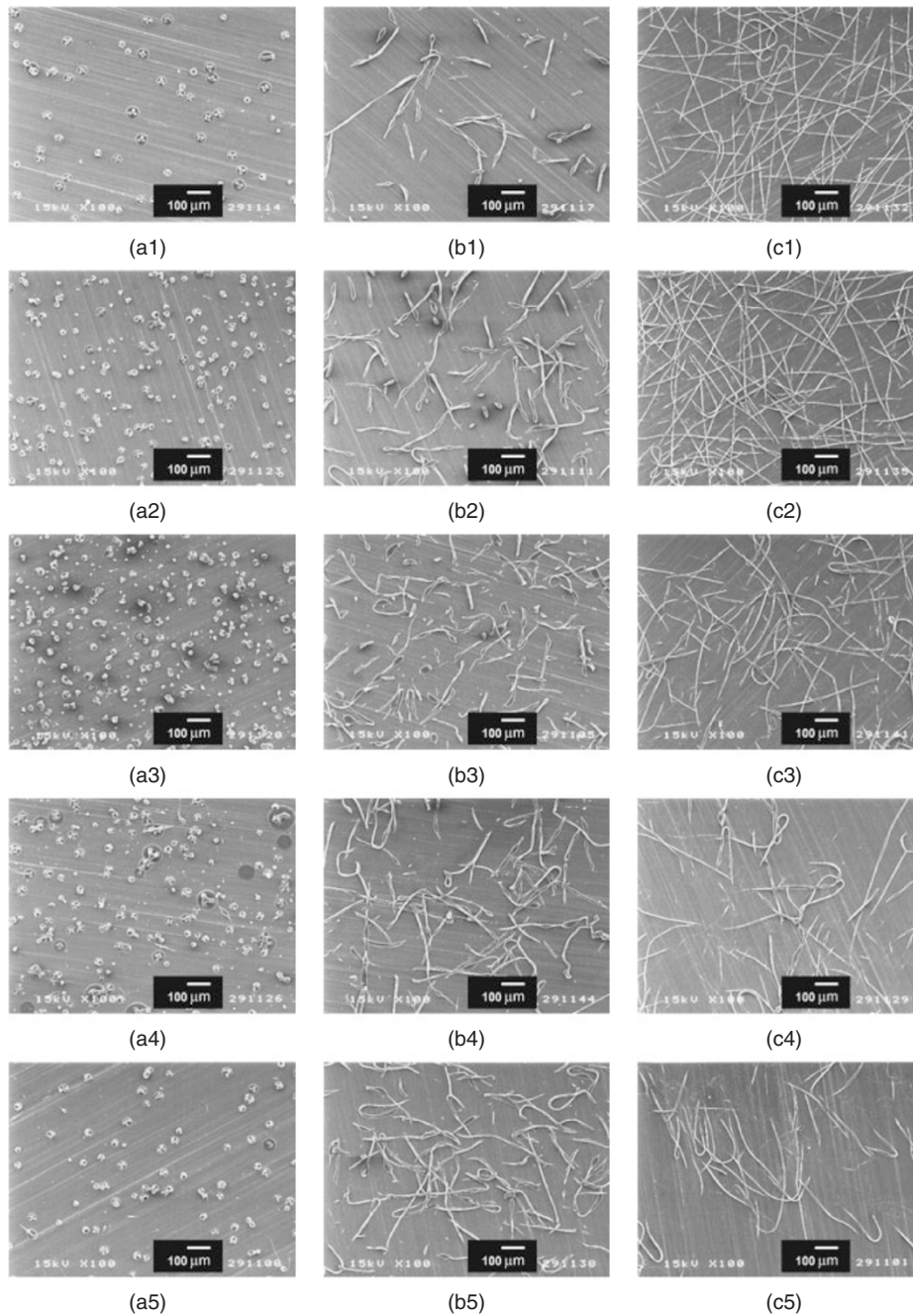


Figure 3. SEM images of the as-spun products from (a) 10, (b) 15, and (c) 20% w/v solutions of PS-PI-PS in 1,2-dichloroethane. “1”, “2”, “3”, “4”, and “5” represent the applied potentials of 5, 7.5, 10, 12.5, and 15 kV, respectively, over a collection distance of 10 cm. The feed flow rate of the solutions was 3 mL/h.

Quantitative results summarized in Tables II–V clearly show that bead density, bead size, and fiber density were all found to decrease with increasing solution concentration, while fiber diameters were the only parameter that was found to increase with increasing solution concentration. This positively confirms the postulation given above. Furthermore, the solution concentration also affects the deposition of the as-spun products (results not shown). With increasing solution concentration, the deposition area was found to decrease and reach a plateau value at some concentrations. The increase in the viscosity of

the solutions should be responsible for such observation, because greater viscosity leads to greater viscoelastic force that is responsible for preventing the charged jet from being stretched.

Effect of Solvent

In order to investigate the effect of solvent on morphological appearance and size of the as-spun products, the as-prepared PS-PI solutions in either 1,2-dichloroethane or chloroform were electrospun. Selected SEM images of the products obtained and quantitative analysis in terms of the physical appearance of the

Table II. Bead density [average number of beads per unit area, #bead/(cm)²] of the as-spun products from PS-PI and PS-PI-PS solutions in 1,2-dichloroethane or chloroform. The applied potentials were varied between 5 and 17.5 kV over a fixed collection distance of 10 cm and the feed flow rate was 3 mL/h

Applied potential (kV)	PS-PI in 1,2-dichloroethane			PS-PI in chloroform			PS-PI-PS in 1,2-dichloroethane		
	10%	15%	20%	10%	15%	20%	10%	15%	20%
	w/v	w/v	w/v	w/v	w/v	w/v	w/v	w/v	w/v
5	90.3 ± 3.6	50.4 ± 5.1	—	n/a	n/a	n/a	n/a	n/a	n/a
7.5	101.7 ± 2.5	120.5 ± 7.6	—	74.7 ± 5.5	17.5 ± 1.9	2.2 ± 1.2	49.5 ± 4.4	42.3 ± 3.6	—
10	142.1 ± 15.3	168.2 ± 9.4	—	95.4 ± 10.2	29.2 ± 3.8	3.1 ± 2.3	115.6 ± 5.4	53.1 ± 2.5	—
12.5	144.8 ± 1.3	36.3 ± 0.5	—	45.0 ± 15.9	29.7 ± 9.5	5.4 ± 6.8	219.5 ± 6.6	76.5 ± 8.5	—
15	109.1 ± 7.0	28.2 ± 3.2	—	39.6 ± 8.5	9.0 ± 10.2	1.8 ± 3.9	138.5 ± 3.1	54.0 ± 6.7	—
17.5	n/a	n/a	n/a	n/a	n/a	n/a	73.8 ± 2.9	48.6 ± 4.7	—

Table III. Bead size (μm) of the as-spun products from PS-PI and PS-PI-PS solutions in 1,2-dichloroethane or chloroform. The applied potentials were varied between 5 and 17.5 kV over a fixed collection distance of 10 cm and the feed flow rate was 3 mL/h

Applied potential (kV)	PS-PI in 1,2-dichloroethane			PS-PI in chloroform			PS-PI-PS in 1,2-dichloroethane		
	10%	15%	20%	10%	15%	20%	10%	15%	20%
	w/v	w/v	w/v	w/v	w/v	w/v	w/v	w/v	w/v
5	66.9 ± 22.5	42.1 ± 12.6	—	n/a	n/a	n/a	n/a	n/a	n/a
7.5	65.8 ± 14.7	35.1 ± 9.2	—	120.4 ± 29.9	44.3 ± 14.2	32.1 ± 2.1	39.6 ± 8.9	16.9 ± 5.2	—
10	54.3 ± 12.0	21.0 ± 7.6	—	110.2 ± 25.7	30.2 ± 7.6	29.7 ± 7.7	28.1 ± 8.8	14.1 ± 2.6	—
12.5	59.6 ± 16.8	25.6 ± 9.4	—	110.1 ± 30.7	29.4 ± 12.2	29.4 ± 13.2	22.2 ± 7.5	13.8 ± 2.6	—
15	55.6 ± 19.8	28.2 ± 8.8	—	109.4 ± 32.2	25.4 ± 13.8	29.3 ± 8.0	35.8 ± 13.5	11.7 ± 3.2	—
17.5	n/a	n/a	n/a	n/a	n/a	n/a	33.3 ± 5.7	10.7 ± 3.6	—

Table IV. Fiber density [average number of fibers per unit area, #fiber/(cm)²] of the as-spun products from PS-PI and PS-PI-PS solutions in 1,2-dichloroethane or chloroform. The applied potentials were varied between 5 and 17.5 kV over a fixed collection distance of 10 cm and the feed flow rate was 3 mL/h

Applied potential (kV)	PS-PI in 1,2-dichloroethane			PS-PI in chloroform			PS-PI-PS in 1,2-dichloroethane		
	10%	15%	20%	10%	15%	20%	10%	15%	20%
	w/v	w/v	w/v	w/v	w/v	w/v	w/v	w/v	w/v
5	—	8.6 ± 1.9	4.2 ± 0.5	n/a	n/a	n/a	n/a	n/a	n/a
7.5	—	20.7 ± 2.5	5.6 ± 1.6	—	9.9 ± 2.6	1.8 ± 1.2	—	—	63.9 ± 1.9
10	—	32.8 ± 4.5	37.3 ± 2.6	—	16.2 ± 1.5	2.7 ± 2.1	—	—	75.6 ± 2.5
12.5	—	6.7 ± 2.1	6.6 ± 2.7	—	27.0 ± 3.5	8.1 ± 3.0	—	—	50.8 ± 1.8
15	—	9.3 ± 1.4	4.5 ± 1.3	—	11.7 ± 1.4	4.5 ± 1.5	—	—	27.9 ± 3.3
17.5	n/a	n/a	n/a	n/a	n/a	n/a	—	—	22.9 ± 1.4

Table V. Fiber diameters (μm) of the as-spun products from PS-PI and PS-PI-PS solutions in 1,2-dichloroethane or chloroform. The applied potentials were varied between 5 and 17.5 kV over a fixed collection distance of 10 cm and the feed flow rate was 3 mL/h

Applied potential (kV)	PS-PI in 1,2-dichloroethane			PS-PI in chloroform			PS-PI-PS in 1,2-dichloroethane		
	10%	15%	20%	10%	15%	20%	10%	15%	20%
	w/v	w/v	w/v	w/v	w/v	w/v	w/v	w/v	w/v
5	—	3.1 ± 1.0	5.1 ± 1.5	n/a	n/a	n/a	n/a	n/a	n/a
7.5	—	3.1 ± 0.9	6.9 ± 1.6	—	4.3 ± 1.3	16.1 ± 2.5	—	—	4.2 ± 1.1
10	—	2.7 ± 0.5	7.9 ± 4.0	—	6.8 ± 1.8	16.0 ± 1.9	—	—	5.8 ± 1.4
12.5	—	5.8 ± 2.7	8.5 ± 1.4	—	5.4 ± 2.0	13.2 ± 3.6	—	—	8.5 ± 2.8
15	—	6.7 ± 2.4	12.3 ± 3.0	—	7.2 ± 2.8	12.4 ± 5.2	—	—	8.5 ± 3.8
17.5	n/a	n/a	n/a	n/a	n/a	n/a	—	—	9.3 ± 2.0

Table VI. Viscosity (mPa s) of the as-prepared PS-PI and PS-PI-PS solutions in 1,2-dichloroethane and chloroform

Copolymer	Concentration (% w/v)	1,2-Dichloroethane	Chloroform
PS-PI	10	125	108
	15	523	487
	20	1407	1294
PS-PI-PS	10	112	n/a
	15	500	n/a
	20	1381	n/a

products are shown in Figures 1 and 2 and summarized in Tables II–V, respectively. Clearly, the as-sprayed beads and the as-spun fibers from PS-PI solutions in chloroform were consistently larger than those from the solutions in 1,2-dichloroethane (see Tables III and V). The greater dielectric constant of 1,2-dichloroethane than that of chloroform (*i.e.*, 10.2 versus 4.8, respectively; see Table I) should be responsible for the observed smaller sizes of the obtained beads and fibers, because greater dielectric constant leads to greater electrostatic force (responsible for carrying the charged jet to the collective target) and Coulombic repulsion force (responsible for the stretching of the charged jet).¹⁸ This was accentuated by the fact that the real density of the as-spun products from PS-PI solutions in 1,2-dichloroethane was consistently greater than that from the solutions in chloroform (see Tables II and IV). Since the feed flow rate was somewhat fixed, the smaller sizes of the obtained beads and fibers would naturally cause the number of these beads and fibers to increase (due to the conservation of mass).

Effect of Applied Potential

In order to investigate the effect of applied potential on morphological appearance and size of the as-spun products, the as-prepared PS-PI and PS-PI-PS solutions were electrospun at various applied electrostatic potentials. Selected SEM images of the products obtained and quantitative analysis in terms of the physical appearance of the products are shown in Figures 1–3 and summarized in Tables II–V, respectively. Evidently, the density of the as-sprayed beads and the as-spun fibers or beaded fibers was generally found to increase with initial increase in the applied potential, reach a maximum at an immediate value, and decrease with further increase in the applied potential. On the contrary, the size of both the beads and the fibers was generally found to either monotonously decrease or initially decrease with increasing applied potential, reach a minimum at an immediate value, and increase with further increasing applied potential.

At a given concentration, the increase in the applied potential could result in an increase in total number of charged species within a jet segment, hence an increase in both the electrostatic and the Coulombic repulsion forces. The increase in the Coulombic repulsion force should be responsible for the observed decrease in the size of both the as-sprayed beads and the as-spun fibers or beaded fibers, while the increase in the electrostatic force could contribute to the observed increase in the size of the as-spun products. The increase in the size of the as-spun products due to the increased electrostatic force should be caused by two different phenomena. The first is due to the decrease in the total path trajectory that the jet travels from the nozzle to the screen collector, a result of the increase in the speed of the jet, while the second is due to the increase in the total feed flow rate. Consequently, whether the as-spun products should be increase or decrease in their size and their deposition area depends totally on the competition between these two effects.

Effect of Chemical Structure

In order to investigate the effect of chemical structure on morphological appearance and size of the as-spun products, the as-prepared PS-PI and PS-PI-PS solutions in 1,2-dichloroethane were electrospun. As previously noted, PS-PI copolymer exhibits a multi-arm structure, while PS-PI-PS copolymer exhibits a linear structure. Both copolymers have a similar molecular weight and a similar weight percentage of PS content in their structures. Despite the difference in their chemical structures, the viscosity of their solutions in 1,2-dichloroethane was essentially the same (see Table VI). Interestingly, despite the observed similarity in the viscosity of the spinning solutions, the electrospinnability of these solutions was totally different (see Figures 1 and 3). With increasing solution concentration, the electrospun products from PS-PI solutions changed from discrete beads, to round spindle-like beaded fibers, and finally to long fibers, while those from PS-PI-PS solutions changed from discrete beads, to worm-like beads, and finally to short fibers (with diameters around 4.2–9.5 μm) with the presence of slight trace of ultrafine fibers (with an average diameter of about 350 nm). Furthermore, the size of the as-sprayed beads and the as-spun fibers from PS-PI solutions was consistently larger than that of the products from PS-PI-PS solutions. Greater number of entanglements and/or greater hydrodynamic volume of PS-PI over that/those of PS-PI-PS could be responsible for such observation.

Effect of Solution Flow Rate

In order to illustrate the effect of the solution flow

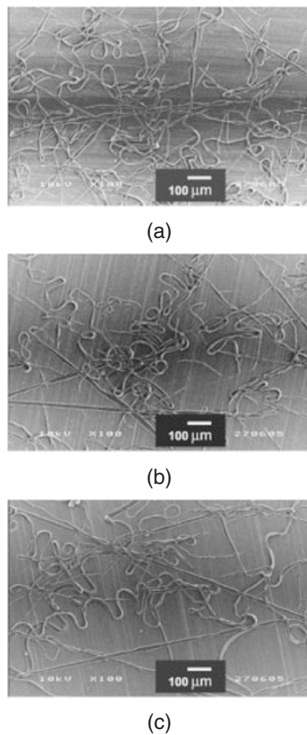


Figure 4. SEM images of the as-spun fibers from 20% w/v PS-PI solution in 1,2-dichloroethane under various feed flow rates of the solutions: (a) 3, (b) 15, and (c) 27 mL/h. The applied potential was 10 kV over a collection distance of 10 cm.

rate on morphological appearance and size of the as-spun products, the solution of 20% w/v PS-PI in 1,2-dichloroethane was electrospun at an applied electrostatic field strength of 10 kV/10 cm at three different solution flow rates. Selected SEM images are shown in Figure 4, while the quantitative analysis of the results is summarized in Table VII. With increasing solution flow rate, the areal density of the fibers was found to decrease monotonously, while the average diameter of the fibers was found to increase.

Surface Morphology of Electrospun Products

The surface morphology of the as-spun products was found to be influenced by the size of the as-spun products themselves. The size of the beads, either in the form of discrete beads or beaded fibers, was gen-

Table VII. Quantitative analysis of the as-spun fibers obtained from 20% w/v PS-PI solution in 1,2-dichloroethane under varying feed flow rate. The applied potential was 10 kV over a fixed collection distance of 10 cm

Feed flow rate (mL/h)	Fiber density [average number of fibers per unit area, #fiber/(cm) ²]	Fiber diameters (μm)
3	37.3 ± 2.6	7.9 ± 4.0
15	24.9 ± 1.7	10.5 ± 4.6
27	21.1 ± 1.6	13.9 ± 6.4

erally larger than that of the fibers. As a result, minute pores were observed on the surface of these large objects (see, for examples, in Figure 5). The formation of minute pores should be a result of microscopic phase separation and subsequent evaporation of the solvent from the solvent-rich phase.

CONCLUSION

Successful electrospinning of two chemically distinct thermoplastic elastomers based on block copolymers of styrene and isoprene [*i.e.*, multi-armed poly(styrene-*b*-isoprene) (PS-PI) and linear poly(styrene-*b*-isoprene-*b*-styrene) (PS-PI-PS)] was reported in this contribution for the first time. Either 1,2-dichloroethane or chloroform was used as the solvent. The effects of solution concentration, solvent, applied electrostatic potential, chemical structure of the thermoplastic elastomers, and solution feed rate on morphological appearance and/or size of the as-electrospun products were investigated. Only discrete beads were obtained at the lowest concentration investigated, while rather smooth fibers were obtained at the highest concentration investigated, implying increased electrospinnability of the solutions with increasing solution concentration. Due to the greater dielectric constant of 1,2-dichloroethane over that of chloroform, the size of the as-spun products from PS-PI solutions in 1,2-dichloroethane was consistently smaller than that of from the solutions in chloroform. The increase in the applied electrostatic potential caused the size of the as-spun products from both types of the polymer

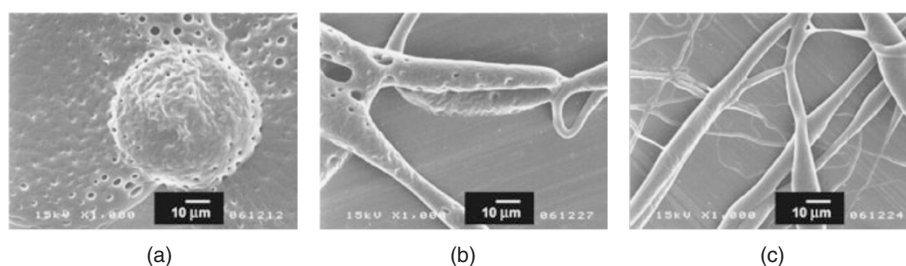


Figure 5. SEM images illustrating the surface morphology of the as-spun products: (a) beads, (b) beaded fibers, and (c) fibers, obtained from 10, 15, and 20% w/v PS-PI solutions in chloroform, respectively.

solutions to decrease monotonously or decrease with initial increase in the applied potential, reach a minimum at an intermediate value, and increase with further increasing applied potential, a result of the competitive effect from the increase in both the electrostatic and the Coulombic repulsion forces. Despite the difference in the chemical structure of the two elastomers, the viscosity of their solutions in 1,2-dichloroethane was essentially similar, but the size of the as-spun products from PS-PI solutions was consistently larger than that of the products from PS-PI-PS solutions. Lastly, the size of the as-spun fibers of both copolymers was found to increase monotonously with increasing the solution feed rate.

Acknowledgment. The authors acknowledge partial support received from 1) the National Research Council of Thailand (NRCT), 2) Chulalongkorn University (through a grant from the Ratchadapesek Somphot Endowment Fund provided to the Conductive and Electroactive Polymers Research Unit), 3) the Petroleum and Petrochemical Technology Consortium [through a Thai governmental loan from Asian Development Bank (ADB)], and 4) the Petroleum and Petrochemical College (PPC), Chulalongkorn University.

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